

# Advanced Global Atmospheric Gases Experiment (AGAGE)

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## INTRODUCTION

Continuous high frequency gas chromatographic measurements of two biogenic/anthropogenic gases ( $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ) and five anthropogenic gases ( $\text{CFCl}_3$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CCl}_3$ ,  $\text{CF}_2\text{ClCFCl}_2$ , and  $\text{CCl}_4$ ) are being carried out at globally-distributed sites in order to quantitatively determine the source and sink strengths and circulation of these chemically and radiatively important long-lived gases. The current station locations are Cape Grim, Tasmania ( $41^\circ\text{S}$ ,  $145^\circ\text{E}$ ), Point Matatula, American Samoa ( $14^\circ\text{S}$ ,  $171^\circ\text{E}$ ), Ragged Point, Barbados ( $13^\circ\text{N}$ ,  $59^\circ\text{W}$ ), and Mace Head, Ireland ( $53^\circ\text{N}$ ,  $10^\circ\text{W}$ ). Stations also previously existed at Cape Meares, Oregon ( $45^\circ\text{N}$ ,  $124^\circ\text{W}$ ) and Adrigole, Ireland ( $52^\circ\text{N}$ ,  $10^\circ\text{W}$ ). The current Mace Head station replaced the Adrigole station and a station is planned at Trinidad Head, California ( $41^\circ\text{N}$ ,  $124^\circ\text{W}$ ) to replace Cape Meares. The program, which began in 1978, is conveniently divided into three parts associated with three changes in instrumentation: the Atmospheric Lifetime Experiment (ALE) that utilized Hewlett-Packard HP5840 gas chromatographs, the Global Atmospheric Gases Experiment (GAGE) that utilizes HP5880 gas chromatographs, and the Advanced (AGAGE) phase that has recently begun using a new fully-automated system from the Scripps Institution of Oceanography (SIO) containing a custom-designed sample module and HP5890 and Carle Instruments gas chromatographic components. Finally, a new Finnigan gas chromatograph-mass spectrometer system for measuring hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons is being installed at Mace Head with another planned for Cape Grim.

## 1993-1994 UPDATE

The data for the seven long-lived gases measured in GAGE during 1993-1994 continue to be generally of

made over the past year as a result of analyzing the data. First, 13 years of ALE/GAGE  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  measurements have been analyzed and published [Cunnold *et al.*, 1994]. Comparisons are made against shipboard measurements made by SIO and archived air samples collected at Cape Grim, Tasmania, since 1978.  $\text{CCl}_3\text{F}$  in the lower troposphere was increasing at an average rate of  $9.2 \text{ ppt yr}^{-1}$  over July 1978 to June 1988.  $\text{CCl}_2\text{F}_2$  was increasing at an average  $17.3 \text{ ppt yr}^{-1}$  in the lower troposphere over the same period. However, between July 1988 and June 1991 the increases of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  in this region have averaged just  $7.0 \text{ ppt yr}^{-1}$  and  $15.7 \text{ ppt yr}^{-1}$ , respectively. The rate of increase has been decreasing  $2.4 \text{ ppt yr}^{-2}$  and  $2.9 \text{ ppt yr}^{-2}$  over this 3-year period. Based on recent scenarios of the worldwide releases of these compounds and using the calibration scale SIO 1993, the equilibrium lifetimes are estimated to be  $44^{+17}_{-10}$  years and  $180^{+820}_{-81}$  years for  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  respectively. Using these lifetime estimates and a two-dimensional model, it is estimated that global releases of these two chlorofluorocarbons (CFCs) in 1990 were  $249 \pm 28 \times 10^6 \text{ kg}$  for  $\text{CCl}_3\text{F}$  and  $366 \pm 30 \times 10^6 \text{ kg}$  for  $\text{CCl}_2\text{F}_2$ . It is also estimated that combined releases of these chlorofluorocarbons in 1990 were  $21 \pm 5\%$  less than those in 1986.

Second, recent analysis of 15 1/2 years of ALE/GAGE  $\text{CH}_3\text{CCl}_3$  data (1978-1993) has shown that global concentrations are decreasing rapidly and are approximately consistent with reported industrial emissions decreases [Prinn *et al.*, 1994]. The concentration decreases (about 12% globally) began in 1991 in the northern hemisphere and in 1992-1993 in the southern hemisphere consistent with the predominantly northern hemisphere industrial emissions and expected interhemispheric mixing times. Interpretation of the data using optimal estimation inverse techniques, together with new SIO 1993 calibrations for this gas and recent estimates of

industrial  $\text{CH}_3\text{CCl}_3$  emissions, indicate a tropospheric lifetime of about 4.85 years which is a significantly lower lifetime than that reported previously [Prinn *et al.*, 1992] that was based on 12 years of data and the old (17% greater) calibration.

Operations at SMO will soon make the transition from the GAGE instrument to the new AGAGE system, with the actual schedule depending upon plans for the replacement of the existing laboratory building at this site. During 1993-1994 the GAGE HP5880 continued to be operated by the CMDL station personnel in collaboration with SIO. Operations were quite smooth and uneventful during this period, with most problems being of a routine maintenance and repair nature. Through the results obtained at SMO where ambient atmospheric water vapor concentrations are high, we have become aware that the quality of the HP5880 electron capture chromatography is sometimes degraded by poor performance of the Nafion drier [Foulger and Simmonds, 1979] configuration used in GAGE, in which pellets of molecular sieve are used to absorb water in the space surrounding the drier tube. As a result, in 1994 we modified all of the GAGE driers to use the same Nafion drier method used for the AGAGE instruments, in which the drier tube is surrounded by a countercurrent flow of dry "zero air."

The new instrument systems for AGAGE represent a significant technological advance. All operations and data acquisition are by a Sun Microsystems workstation computer using custom runfile architecture, signal processing and integration routines, and storing all the data and chromatograms digitally. The instrument measures its own non-linearity for all the AGAGE gases on a regular basis using a pressure-programmed constant-volume injection system and a single gas standard. All channels of the instrument are fitted with precolumns to avoid column contamination by late-eluting gases, and as a result the frequency of measurement has been increased three-fold versus GAGE. Precision is also greatly improved over the GAGE instruments with  $1\sigma$  relative precisions on the order of 0.05% for the rapidly eluting gases  $\text{CH}_4$ ,  $\text{CCl}_2\text{F}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{CCl}_3\text{F}$ . The system works interactively with its uninterruptible power supply so that controlled shutdown and startup of the entire instrument and sampling system are assured when there are extended power outages. The new AGAGE instruments are now operational at Cape Grim and at Mace Head, and the remaining instruments will be installed at the other stations within the coming year.

Another major component of the AGAGE program is the development of new absolute calibration scales. This work is being done using an extension of the "bootstrap" calibration method used earlier at SIO. In the AGAGE work, an all-metal high-vacuum system is used to mix gravimetrically determined aliquots of pure CFCs with about 12 L of gravimetrically determined pure nitrous

oxide. This mixture is prepared at roughly the ambient atmospheric mole ratios of these gases. A small aliquot ( $\sim 0.4 \text{ cm}^3$ ) of this mixture is then introduced using a separate pressure/vacuum system, fitted with a high-pressure chromatographic sampling valve, into a 35-L electropolished stainless steel canister to which about 10 torr of water vapor has been added to reduce wall reactions and adsorption. The canister is then filled with about 40 atmospheres of re-purified "zero air" to bring the nitrous oxide mole fraction to a near-ambient value. The resulting nitrous oxide concentration is then calibrated gas chromatographically against existing SIO standards, and the CFC concentrations are determined by multiplying the measured nitrous oxide mole fraction by the gravimetric CFC nitrous oxide ratios of the original mixture. In this way, we have been able to obtain improved accuracy for all AGAGE gases, but especially for the lower vapor pressure and more adsorptive gases. AGAGE and CMDL are now engaged in an active intercalibration program for all the AGAGE gases as well as for methyl halides and some HCFCs.

## DATA ACCESS

The ALE/GAGE/AGAGE data are archived at the DOE Carbon Dioxide Information Analysis Center at Oak Ridge and are available to interested scientists. Potential users of the data should contact CDIAC (Internet: CDP@ORNL.GOV).

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